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## **ORIGINAL ARTICLE**

# Efficient separation and recovery of V(V) from Cr (VI) in aqueous solution using new task-specific ionic liquid of $[C_{12}H_{25}NH_3][Cyanex 272]$



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#### KEYWORDS

Ionic liquids; Extraction; Recovered NH<sub>4</sub>VO<sub>3</sub>; Separation of V(V) from Cr (VI); Extraction mechanism **Abstract** An environmentally friendly process for efficient separation and recovery of V(V) from aqueous solution containing Cr(VI) was proposed using the new task-specific ionic liquid of  $[C_{12}H_{25}NH_3][Cyanex 272]$ . The separation factor of V(V) from Cr(VI) was about  $1.08 \times 10^3$  with the optimum extraction conditions, and the extraction percentage of V(V) was about 99.5 %. The loaded organic phase was stripped using the NH<sub>3</sub>·H<sub>2</sub>O, and the recovered NH<sub>4</sub>VO<sub>3</sub> was obtained with the processes of stripping, filtration, washing, and desiccation. The qualitative analysis of the recovered NH<sub>4</sub>VO<sub>3</sub> was made using the X-ray diffraction, and its peaks were good consistent with the standard sample. Morphology of the recovered NH<sub>4</sub>VO<sub>3</sub> was also studied using the scanning electron microscope. The extraction mechanism of V(V) using the  $[C_{12}H_{25}NH_3][Cyanex 272]$  was investigated using the slope method and infrared spectrum analysis. This new environmentally friendly process can be used for the separation and recovery of V(V) from real leaching solution with the aim of industrial application.

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#### 1. Introduction

Vanadium is a strategic metal that can be used in different fields, e.g. catalysis, batteries, advanced materials, and alloys (Liu et al., 2015, Zhang et al., 2016). It is widely used for industrial application owing to its excellent physicochemical properties such as tensile strength, corrosion resistance, and fatigue resistance (Liu et al., 2013). In addition, large amounts of industrial waste residue containing vanadium and other metal ions may cause environmental pollution (Hui et al.,

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2020). Recycling of vanadium from this industrial solid waste is very significant to efficiently avoid the environmental pollution and meet the increasing demand of application of vanadium (Ying et al., 2022). The vanadium-bearing chromium slag (V-Cr slag) is a kind of industrial waste residue, and the efficient separation of V(V) from Cr (VI) in aqueous solution is significant to obtain the high-purity  $V_2O_5/NH_4VO_3$  from this secondary waste resources (Ning et al., 2016, Jing et al., 2017a, 2017b). The products of  $V_2O_5/NH_4VO_3$  can be utilized for industrial catalysis and lithium batteries (Garcia et al., 2005, Peng et al., 2016). To the industrial leaching solution of V-Cr slag in China, the concentrations of V(V) and Cr(VI) were about 23.70 g/L and 1.52 g/L, and the high-purity of  $NH_4VO_3$  has been obtained using the multistage counter-current extraction and stripping (Jing et al., 2017a, 2017b).

As a matter of fact, the complete separation of V(V) from Cr(VI) is a complex job due to their similar physicochemical property (Hu et al., 2014a, 2014b, Guo et al., 2020). To separate (V) from aqueous solution containing Cr(VI), several methods have been reported in published papers, e.g. solvent extraction (Sun et al., 2017, Guo et al., 2020), ion exchange (Fan et al., 2013, Li et al., 2016) and absorption (Zhang et al., 2017, Peng et al., 2020). The ion exchange is not efficient to separate two metal ions for the aqueous solution containing high concentration of V(V) and Cr(VI) due to the limited adsorption ability of exchange resins (Guo et al., 2020). The absorption is an efficient method for separation of V(V) from Cr(VI) in the wastewater with low concentration of V(V) and other metal ions, but not for the recovery of V(V) in the real leaching solution with high concentration of metal ions (Liao et al., 2008). Typical extractants (Table 1) have been investigated for the separation of V(V) from Cr(VI) according to published papers. From the Table 1, typical organic extractants including and N235(Ye et al., 2018), sulfated N1923(Jing et al., 2017a, 2017b), and primary amine LK-N21(Ning et al., 2014) were used to separation of V(V) from Cr(VI) in aqueous solution, and the best separation factor of V(V) from Cr(VI) ( $\beta_{V/Cr}$ ) was reached about  $+\infty$  using the extractant of N235. In other words, when N235 used as an extraction agent, the two metal ions can be separated completely under the threestage extraction. However, the solvent extraction process using organic extractants for the recovery of V(V) from aqueous solution containing Cr(VI) has several drawbacks, e.g. volatilization of organic extractant (Marsousi et al., 2018), and degradation of the organic phase (Jing et al., 2018). For example, a fire broke out at Iron & Steel Rare Earth Company of China, and it took this company nearly-four months to restore normal operations (Chen 2016). The employ of large amounts of organic solvent for the separation process was a major reason of the fire. The heavy use of common organic extractants for solvent extraction may lead to the environmental problems and the rising cost of recovery (Wellens et al., 2012, Sobekova Foltova et al., 2019).

Task-specific ionic liquid (TSIL) can be used in solvent extraction for separating metal ions (Jamali et al., 2012, Mohammadzadeh et al., 2020) owing to their unique properties, i.e. high dissolving capability, low vapor pressure, designable structure, and chemical stability (Zakeri et al., 2019). If the TSIL can be used for the efficient separation of the two metal ions, the process of solvent evaporation to the environment will be drastically decreased (Muhammad et al., 2022), and the degradation of organic extractants in the separation process will also be effectively reduced. Therefore, the TSIL (Table 1) of [C<sub>8</sub>mim] [PF<sub>6</sub>] (Hu et al., 2014a, 2014b), [A336][NO<sub>3</sub>] (Zhao et al., 2015a, 2015b), and [RNH<sub>3</sub>][NO<sub>3</sub>] (Zhao et al., 2015a, 2015b) were used for the extraction and separation of the two metal ions. In two TSILbased extraction systems, the values of  $\beta_{V/Cr}$  are 100.6 and 35.0 under their optimum operating conditions. How to develop a new and efficient ionic liquid extraction agent to achieve efficient separation of V (V) from Cr(VI) is one of the focus of current research.

In this research, the new TSIL of  $[C_{12}H_{25}NH_3]$ [Cyanex 272] for the separation of V(V) from Cr(VI) was synthesized using organic acidbase reflux reaction. Their purities were analyzed using Nuclear magnetic resonance hydrogen spectroscopy (<sup>1</sup>H NMR), nuclear magnetic resonance carbon spectroscopy (<sup>13</sup>C NMR), and infrared spectrum (IR spectrum) of TSIL. The optimization of extracted conditions for the separation and recovery of V(V) from Cr(VI) were examined by single-factor experiments. In addition, the extraction mechanism was also investigated using the slope method and IR spectrum analysis according to the published papers. Using the TSIL as an extraction agent will provide an alternative way for environmentally friendly separation and recovery of the two metal ions.

#### 2. Materials and methods

#### 2.1. Chemicals

The simulated aqueous solution containing V(V) and Cr(VI) was made by dissolving NaVO<sub>3</sub>(0.47 mol, 59.31  $\pm$  0.01 g) and Na<sub>2</sub>CrO<sub>4</sub>·4H<sub>2</sub>O(0.038 mol, 8.89  $\pm$  0.01 g) in 1000 mL ultrapure water. The concentrations of V(V) and Cr(VI) in

**Table 1**Typical extractants for the separation of V(V) from Cr(VI).

Extractants	Diluent	Aqueous solution	Extraction effect and operating conditions
N235 (Ye et al., 2018)	Sulfonated kerosene	Sulfuric acid leaching liquor	$E_{\rm V} = 98.24$ %, $E_{\rm Cr} \approx 0.0$ %, $\beta_{\rm V/Cr} \approx +\infty$ ; Three-stage extraction, $C_0 = 10$ vol%, $t_{\rm e} = 15$ min, O/A = 1:2.5, pH <sub>ini</sub> = 1.8-2.0
Sulfated N1923 (Jing et al., 2017)	Sulfonated kerosene	Sulfuric acid leaching liquor	$E_{\rm V} = 99.6$ %, $E_{\rm Cr} = 47.6$ %, $\beta_{\rm V/Cr} = 273.9$ ; Four-stage countercurrent extraction, $C_0 = 15$ vol%, $t_{\rm e} = 4.8$ min, $T_{\rm e} = 298.15$ K, O/A = 1:1, pH <sub>ini</sub> = 5.0
Primary amine LK-N21 (Ning et al., 2014)	Kerosene	Sulfuric acid leaching liquor	$E_{\rm V} = 98.0$ %, $E_{\rm Cr} = 3.14$ %, $\beta_{\rm V/Cr} = 1531$ ; Single-stage extraction, $C_0 = 0.1$ mol/L, $t_{\rm e} = 15$ min, $T_{\rm e} = 291$ K, O/A = 1:1, pH <sub>ini</sub> = 8.50, pH <sub>eq</sub> = 7.70
[C <sub>8</sub> mim][PF <sub>6</sub> ](Hu et al., 2014a, 2014b)		Sulfuric acid leaching liquor	$\beta_{\rm V/Cr}$ = 100.6; Single-stage extraction, pH <sub>eq</sub> = 3.5
[A336][NO <sub>3</sub> ]+ [RNH <sub>3</sub> ][NO <sub>3</sub> ](Zhao et al., 2015a, 2015b)		Nitric acid aqueous solution	$\beta_{V/Cr} = 35.0$ ; Single-stage extraction, 0.3 mL [A336][NO <sub>3</sub> ] and 0.2 mL [RNH <sub>3</sub> ] [NO <sub>3</sub> ], $C_{V(V)} + C_{Cr(VI)} = 19.6 \text{ mmol/l}, \text{ pH}_{eq} = 9.0$

(N235 is trialkylamine;  $E_V$  is extraction percentage of V(V);  $E_{Cr}$  is extraction percentage of Cr(VI);  $C_0$  is the concentration of extractant;  $t_e$  is the extraction time;  $T_e$  is the extraction temperature; O/A is the volume ratio of organic phase to aqueous phase; pH<sub>ini</sub> is the initial pH of aqueous solution; pH<sub>eq</sub> is the equilibrium pH of aqueous solution; N1923 is primary amine; LK-N21 is an extractant of primary amine; [C<sub>8</sub>mim][PF<sub>6</sub>] is 1-octyl-3-methylimidazolium hexafluorophosphate).

the aqueous solution were 23.70 g/L and 1.95 g/L, respectively. The concentrations of two metal ions were in accordance with values of the leaching solution from V-Cr slag (Jing et al., 2017a, 2017b). The source and mass fraction of chemicals used for the experiments were listed in Table 2. The water was ultrapure water, and its specific resistance is more than 18.2 M $\Omega$ ·cm (Millipore Milli-Q). The synthesized [C<sub>12</sub>H<sub>25</sub>NH<sub>3</sub>][Cyanex 272] and sulfonated kerosene were used for the extractant and diluting agent.

#### 2.2. Synthesis of $[C_{12}H_{25}NH_3][Cyanex 272]$

The organic acid-base reflux reaction of Cyanex 272 (20.00  $\pm$  0.01 g, 68.9 mmol) and C<sub>12</sub>N<sub>25</sub>NH<sub>2</sub> (12.80  $\pm$  0.01 g, 68.9 mmol) was carried out in anhydrous ethanol (Fig. 1). The reaction temperature was 365.2  $\pm$  0.1 K, the reaction time was 210 min, and the reaction pressure was ordinary pressure. When the reaction was finished, the organic phase was dehydrated using anhydrous sodium sulfate, and the TSIL of [C<sub>12</sub>H<sub>25</sub>NH<sub>3</sub>][Cyanex 272] was obtained by treating the organic phase with rotary evaporator. The yield of [C<sub>12</sub>H<sub>25</sub>NH<sub>3</sub>][Cyanex 272] was approximately 93.5 wt% (taking the Cyanex 272 being a reference).

#### 2.3. Instrument analysis

A pH meter (Mettler Toledo, Switzerland, Delta320) with a combined glass electrode was used to measure the acidity of the aqueous phase. The concentrations of metal ions in the aqueous phase were determined using an inductive couple plasma-optical emission spectrometry (PerkinElmer, United States, ICP-OES, Optima 8000). The <sup>1</sup>H and <sup>13</sup>C NMR of synthetic TSIL were analyzed using a nuclear magnetic resonance spectrometer (Bruker, Switzerland, Avance III 400 MHz). The

IR spectra of TSIL and extracted complex were tested by a fourier transform infrared spectroscope (Spectrum Two N, PerkinElmer, United States). Phase identification of recovered NH<sub>4</sub>VO<sub>3</sub> was made using an X-ray diffractometer (XRD) with Cu Ka radiation (Rigaku Corporation, Japan, Smartlab). Morphology of powder was analyzed using a high-resolution cold-field emission-based scanning microscopy (SEM, SU8010, Hitachi, Japan).

#### 2.4. Liquid-liquid extraction and stripping process

Single-factor extracted experiments were performed by mixing 10 mL aqueous phase and 20 mL organic phase in a separating funnel. The organic phase was consisted of extractant (i.e. [C<sub>12</sub>H<sub>25</sub>NH<sub>3</sub>][Cyanex 272]) and diluent (i.e. sulfonated kerosene). The initial pH of the aqueous phase (pH<sub>ini</sub>) was adjusted using diluted sulfuric acid or NaOH solution. A mixture of two insoluble phases was reacted in an oscillating water bath (SHA-C, Jie Ruier, China). When the extracted reaction was completed, two mixed phases were still and stratified under the action of gravity. The loaded organic phase containing V (V) and a trace of Cr(VI) was obtained from the upper layer of the separating funnel, and the raffinate (i.e. aqueous solution) was got from the lower layer of the funnel. A pH meter was used to measure the pH<sub>ini</sub> and the equilibrium pH of raffinate. The ICP-OES was used to analyse the concentrations of metal ions in the aqueous phase.

The loaded organic phase containing V(V) and a trace of Cr (VI) was scrubbed twice using fresh water with scrubbing time of 10 min, a volume ratio of loaded organic phase to the aqueous phase of 1: 1, and scrubbing temperature of  $298.2 \pm 0.1$  K. The loaded organic phase was then stripped with diluting NH<sub>3</sub>·H<sub>2</sub>O solution. Unless otherwise stated, all single-factor experiments including extraction and stripping were repeated

 Table 2
 Source and purity of chemicals used in the work.

Chemicals	Source	Mass fraction/% (%)		
Na <sub>2</sub> CrO <sub>4</sub> ·4H <sub>2</sub> O	Adamas Reagent Co., ltd (Switzerland)	99.0		
NaVO <sub>3</sub>	Adamas Reagent Co., ltd (Switzerland)	≧99.0		
$H_2SO_4$	Luoyang Chemical Reagent Factory (China)	95.0-98.0		
Cyanex 272	Guangdong Wengjiang Chemical Reagent Co., ltd (China)	≧99.0		
$C_{12}N_{25}NH_2$	Shanghai Titan Scientific Co., ltd (China)	$\geq 98.0$		
C <sub>2</sub> H <sub>5</sub> OH	Tianjin Fuyu Fine Chemical Co., ltd (China)	≧99.0		
Sulfonated kerosene	Guangdong Wengjiang Chemical Reagent Co., ltd (China)			
NH <sub>3</sub> ·H <sub>2</sub> O	Shanghai Titan Scientific Co., ltd (China)	25.0-28.0		
NaOH	Shanghai Titan Scientific Co., ltd (China)	$\geq 98.0$		
Na <sub>2</sub> SO <sub>4</sub>	Shanghai Titan Scientific Co., ltd (China)	≧99.0		

bis(2,4,4-trimethylpentyl)phosphinic acid Chemical Formula: C<sub>16</sub>H<sub>35</sub>O<sub>2</sub>P



Fig. 1 Synthetic reaction of  $[C_{12}H_{25}NH_3]$ [Cyanex 272].

three times under ordinary pressure, and their average value was used for plotting or analyzing the reaction mechanism.

#### 2.5. Formulas

Extraction percentages of V(V) ( $E_V$ ), Cr(VI) ( $E_{Cr}$ ), and the separation factor ( $\beta_{V/Cr}$ ) of V(V) from Cr(VI), distribution coefficient of V(V) ( $D_V$ ), the stripping percentage of V(V) ( $S_V$ ), were calculated as Eqs. (1)–(5).

$$E_V = \frac{V_1 C_{1(V)} - V_2 C_{2(V)}}{V_1 C_{1(V)}} \times 100$$
(1)

$$E_{Cr} = \frac{V_1 C_{1(Cr)} - V_2 C_{2(Cr)}}{V_1 C_{1(Cr)}} \times 100$$
<sup>(2)</sup>

$$\beta_{V/Cr} = \frac{E_V \times (100 - E_{Cr})}{(100 - E_V) \times E_{Cr}}$$
(3)

$$D_V = \frac{E_V}{1 - E_V} \tag{4}$$

$$S_V = \frac{V_E \times C_{E(V)} + m_1 \times \frac{50.94}{116.98}}{V_1 C_{1(V)} \times E_V} \times 100$$
(5)

where  $V_1$  and  $V_2$  (L) represent the volumes of the stock and raffinate phase, respectively.  $C_{1(V)}$  and  $C_{2(V)}$  (g/L) represent the concentrations of V(V) in the stock and raffinate phases.  $C_{1(Cr)}$  and  $C_{2(Cr)}$  represent the concentrations of Cr(VI) in the stock and raffinate phases.  $V_E$  (L) represents the volume of stripping phase, and  $C_{E(V)}$  (g/L) represents the concentration of V(V) in the stripping phase. The  $m_1$  (g) represent the quality of recovered NH<sub>4</sub>VO<sub>3</sub>.

#### 3. Results and discussion

# 3.1. NMR and IR spectrum analysis of $[C_{12}H_{25}NH_3][Cyanex 272]$

The real figures of Cyanex 272, C<sub>12</sub>H<sub>25</sub>NH<sub>2</sub>, and [C<sub>12</sub>H<sub>25</sub>NH<sub>3</sub>] [Cyanex 272] are shown in Fig. 2a. The Cyanex 272 and [C<sub>12</sub>H<sub>25</sub>NH<sub>3</sub>][Cyanex 272] are liquid, but the C<sub>12</sub>H<sub>25</sub>NH<sub>2</sub> is a solid body. The <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) of [C<sub>12</sub>H<sub>25</sub>NH<sub>3</sub>][Cyanex 272] is shown in Fig. 2b, and the specific spectrum analysis is as follows:  $2.72(t, 2H, CH_2, J = 16 Hz)$ , 1.87(d, 2H, CH<sub>2</sub>), 1.67(s, 2H, CH<sub>2</sub>), 1.59(d, 2H, CH<sub>2</sub>), 1.40(m, 2H, 2 × CH), 1.25(m, 22H, 11 × CH<sub>2</sub>), 1.11(m, 9H,  $2 \times CH_3 + 1 \cdot NH_3$ , 0.88(t, 21H, 7 × CH<sub>3</sub>, J = 20 Hz). The <sup>1</sup>C NMR (400 MHz, CDCl<sub>3</sub>, ppm) of [C<sub>12</sub>H<sub>25</sub>NH<sub>3</sub>][Cyanex 272] is shown in Fig. 2c, and the displacements of carbon are resolved as follows: 14.13, 22.70, 23.95, 23.99, 24.26, 24.31, 25.71, 27.04, 29.37, 29.64, 29.66, 30.31, 30.33, 31.18, 31.92, 40.14, 40.89, 41.02, 41.76, 53.39, 53.50, 53.77, 53.89. The IR spectrum of [C<sub>12</sub>H<sub>25</sub>NH<sub>3</sub>][Cyanex 272] is shown in Fig. 2d, and characteristic peaks are analyzed as follows: asymmetric stretching vibration of -CH<sub>2</sub> (2923 cm<sup>-1</sup>), symmetric stretching vibration of -CH<sub>3</sub> (2854 cm<sup>-1</sup>) (Suresh et al., 2016), inplane bending vibration of  $-CH_2$  (1467 cm<sup>-1</sup>), in-plane bend-ing vibration of  $-CH_3$  (1363 cm<sup>-1</sup>) (Tayyari et al., 2016), bending vibration of P=O (1132 cm<sup>-1</sup>) (Frost et al., 2013), stretching vibration of C-C(1022 cm<sup>-1</sup>) (Zhao et al., 2015a, 2015b).

#### 3.2. Effect of $pH_{ini}$ on $E_v$ and $\beta_{V/Cr}$

The equilibrium pH of the aqueous phase is one of the crucial factors affecting the extraction efficiency of metal ions (Hu et al., 2014a, 2014b). For example, the  $E_V$  increase gradually using extractant of Mextral 973H when the equilibrium pH ranges from -0.8 to 1.5 (Zhang et al., 2018). Compared with the single extractant (Zhang et al., 2016), synergistic extractant of Aliquat 336 and TBP have a wider range of equilibrium pH for the separation of V(V). In the extraction of V(V) using the LIX63 and PC88A, the pH<sub>ini</sub> was ranged from 1.2 to 6.0 when the equilibrium pH was varied from 1.6 to 5.4 (Nguyen and Lee, 2015). Therefore, the equilibrium pH is determined by its pH<sub>ini</sub> in the same extraction system. In addition, the pH<sub>ini</sub> is easy to adjust in real experiments or industrial application.

Therefore, in this study, the effect of  $pH_{ini}$  on  $E_V$ ,  $E_{Cr}$ , and  $\beta_{V/Cr}$  is shown in Fig. 3 with the operating conditions of the volume ratio of organic phase to aqueous phase (O|A) is 2:1, the concentration of  $[C_{12}H_{25}NH_3]$ [Cyanex 272] (C<sub>1</sub>) is 0.24 mol/L, extraction time ( $t_e$ ) is 35 min, and extraction temperature ( $T_e$ ) is 298.2  $\pm$  0.1 K is shown in Fig. 3. The pH<sub>ini</sub> of the aqueous phase is difficult to accurately adjust to a fixed value, therefore, the range of  $pH_{ini}$  error is set to  $\pm 0.02$ (Fig. 3a). From images of partial extraction experiments, the phase interface is distinct after oscillation reaction and static layering. The  $E_V$ ,  $E_{Cr}$ , and  $\beta_{V/Cr}$  decrease when pH<sub>ini</sub> ranges from 1.5 to 5.0 (Fig. 3b). When the pH<sub>ini</sub> are 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0, the average of  $E_V$  from the three parallel trials are 98.7, 85.4, 77.5, 74.1, 69.4, 66.4, 54.8, 45.3 %, and the  $E_{Cr}$  are 7.2, 6.1, 5.3, 4.9, 4.6, 4.1, 3.8, 3.6, and the  $\beta_{V/Cr}$  are 1077.9, 89.9, 61.6, 55.6, 47.0, 46.3, 30.7, 22.5. When  $pH_{ini} = 1.5$ , the  $E_V$  and  $\beta_{V/Cr}$  are larger than the values under the other  $pH_{ini}$ . Therefore, the  $pH_{ini} = 1.5$  is a reasonable extractive condition for the efficient separation of V(V) from Cr(VI) in the subsequent studies.

#### 3.3. Effect of $C_1$ on $E_V$ and $\beta_{V/Cr}$

The  $C_1$  were set as 0.17, 0.19, 0.22, 0.24, 0.26, 0.29, and 0.31 mol/L, and the concentration of V(V) ( $C_V$ ) in the aqueous solution was 0.47 mol/L. The proportions of  $C_1$  to  $C_V$  were 0.36, 0.40, 0.46, 0.51, 0.55, 0.62, and 0.66. The effect of  $C_1$ on  $E_V$ ,  $E_{Cr}$ , and  $\beta_{V/Cr}$  using  $[C_{12}H_{25}NH_3]$ [Cyanex 272] dissolved in sulfonated kerosene is shown in Fig. 4 under the conditions of pH<sub>ini</sub> = 1.5, O/A = 2:1,  $t_e = 35$  min, and  $T_e = 298$ .  $2 \pm 0.1$  K. The  $E_{\rm V}$  and  $E_{\rm Cr}$  increase with the growth of  $C_1$ , but the  $\beta_{V/Cr}$  first increase and then decrease with the increasing of the C<sub>1</sub>. The  $E_V$  and  $\beta_{V/Cr}$  are 99.5 and 1.07  $\times$  10<sup>3</sup> when  $C_1 = 0.26 \text{ mol/L}$ . The extractive stoichiometry of V(V) using  $[C_{12}H_{25}NH_3]$ [Cyanex 272] can be expressed as Eq. (6) (Ning et al., 2014), AB represents the [C<sub>12</sub>H<sub>25</sub>NH<sub>3</sub>][Cyanex 272], the main species of V(V) in the range of equilibrium pH is  $V_4 O_{12}^{4-}$ , and y represents the coefficient of the chemical reaction equation.

$$y(AB)_{(org)} + V_4 O_{12(aq)}^{4-} + 4H_{(aq)}^+ \rightleftharpoons (AB)_y \cdot (H_4 V_4 O_{12})$$
(6)

According to Eq. (6), increasing the  $C_1$  can promote the degree of extractive reaction. Therefore,  $E_V$  increases as  $C_1$  increases, and this conclusion is consistent with the experiment results. However, the  $\beta_{V/Cr}$  is determined by the  $E_V$  and  $E_{Cr}$ ,



**Fig. 2** Images of Cyanex 272,  $C_{12}H_{25}NH_2$ , and  $[C_{12}H_{25}NH_3]$ [Cyanex 272](a); <sup>1</sup>H NMR (b) and <sup>13</sup>C NMR (c) of  $[C_{12}H_{25}NH_3]$ [Cyanex 272]; IR spectrum of  $[C_{12}H_{25}NH_3]$ [Cyanex 272](d).



Fig. 3 Images of partial extraction experiments (a); Effect of pH<sub>ini</sub> on  $E_v$  and  $\beta_{V/Cr}$  (b).



**Fig. 4** Effect of  $C_1$  on  $E_v$  and  $\beta_{V/Cr.}$ 

and its maximal value is  $1.07 \times 10^3$  when  $C_1 = 0.26$  mol/L. Therefore, the  $C_1$  of 0.26 mol/L is the suitable condition for the efficient separation for V(V) from Cr(VI).

#### 3.4. Effect of $t_e$ on $E_V$ and $\beta_{V/Cr}$

When  $pH_{ini} = 1.5$ , O/A = 2.1,  $C_1 = 0.26 \text{ mol/L}$ , and  $T_e =$ 298.2  $\pm$  0.1 K, the effect of  $t_e$  on  $E_v$ ,  $E_{Cr}$  and  $\beta_{V/Cr}$  using the extractant of [C<sub>12</sub>H<sub>25</sub>NH<sub>3</sub>][Cyanex 272] is shown in Fig. 5. The  $E_{\rm v}$ ,  $E_{\rm Cr}$  and  $\beta_{\rm V/Cr}$  are increased with the growth of  $t_e$ . When  $t_e$  are 25, 30, and 35 min, the  $E_V$  are 99.5, 99.5, and 99.5 %, and the  $E_{Cr}$  are 15.6, 15.8, and 15.7 %, and the  $\beta_{\rm V/Cr}$  are 1.08  $\times$  10<sup>3</sup>, 1.05  $\times$  10<sup>3</sup>, and 1.07  $\times$  10<sup>3</sup>. Extracted reaction of vanadium using extractants of N235 reaches an equilibrium state within 5 min because that the little change of  $E_v$  is made when the  $t_e$  exceeds 5 min (Ye et al., 2018). For example, extraction of V(IV) using the synergistic extractant of D2EHPA and PC88A reaches an equilibrium in 12 min due to the slight change as the  $t_e$  is prolonged from 12 to 16 min (Shi et al., 2017). In this study, The  $E_v$ , and  $\beta_{V/Cr}$  are not changed or changed less when  $t_e$  are 25, 30, and 35 min. and the extractive reaction can be reached equilibrium state when  $t_e = 25$  min. Therefore,  $t_e = 25$  min is an appropriate extractive time for separation of V(V) from Cr(VI). The best  $\beta_{\rm V/Cr}$  is 1.08  $\times$  10<sup>5</sup> using the new TSIL with the optimum oper-



**Fig. 5** Effect of  $t_e$  on  $E_v$  and  $\beta_{V/Cr.}$ 

ating conditions, which is better than the values of  $\beta_{V/Cr}$  for [C<sub>8</sub>mim][PF<sub>6</sub>] (Hu et al., 2014a, 2014b), [A336][NO<sub>3</sub>] (Zhao et al., 2015a, 2015b), and [RNH<sub>3</sub>][NO<sub>3</sub>] (Zhao et al., 2015a, 2015b). In other words, the TSIL of [C<sub>12</sub>H<sub>25</sub>NH<sub>3</sub>][Cyanex 272] is a good extractant for recovery and separation of V (V) from Cr(VI).

#### 3.5. Extraction mechanism for the separation of V(V)

The stoichiometry of extracted reaction can be determined using the slope method (Jiang et al., 2015, Li et al., 2020), and extracted reaction using  $[C_{12}H_{25}NH_3][Cyanex 272]$  for V (V) can be expressed as Eq. (7) (Ning et al., 2014).

$$x[C_{12}H_{25}NH_3][Cyanex272]_{(org)} + V_4O_{12(aq)}^{4-} + 4H^+ \times \ \rightleftharpoons [C_{12}H_{25}NH_3][Cyanex272]_x \cdot (H_4V_4O_{12})_{(org)}$$
(7)

For Eq. (7), the equilibrium constant  $K_{ex}$  is expressed as:

$$K_{\rm ex} = \frac{C_6}{C_3^x \cdot C_4 \cdot C_5^4}$$
(8)

1

where  $C_3$ ,  $C_4$ ,  $C_5$ , and  $C_6$  represent the concentration of  $[C_{12}H_{25}NH_3][Cyanex 272]$ ,  $[V_4O_{12}]^4$ ,  $H^+$ , and  $[C_{12}H_{25}NH_3]$  [Cyanex 272]· $(H_4V_4O_{12})$  in the aqueous or organic phase. The Eq. (8) can be further expressed as:

$$K_{ex} = \frac{D_V}{C_3^x \cdot C_5^4}$$
(9)

The form of Eq. (9) is changed by taking logarithm:

$$\log D_V = x \log C_3 + \log K_{ex} - 4pH_{eq} \tag{10}$$

$$\log D_V + 4pH_{eq} = x\log C_3 + \log K_{ex} \tag{11}$$

where  $pH_{eq}$  indicates the equilibrium pH value in the raffinate. The value of × in the Eq. (11) can be determined by the slope method (Fig. 6). The × is about 4.03, and it value is approximately 4.0. Therefore, the equation of the chemical reaction can be listed as Eq. (12).

$$4[C_{12}H_{25}NH_3][Cyanex\ 272]_{(org)} + V_4O_{12(aq)}^{4-} + 4H^+ \times \Leftrightarrow [C_{12}H_{25}NH_3][Cyanex\ 272]_4 \cdot (H_4V_4O_{12})_{(org)}$$
(12)

In order to further study the extractive mechanism, the powder of the  $[C_{12}H_{25}NH_3]$  [Cyanex 272]<sub>4</sub>·H<sub>4</sub>V<sub>4</sub>O<sub>12</sub> (Fig. 7) was obtained using the process of solvent-out crystallization (Zhao et al., 2019). The solvent-out crystallization was listed as follows: (1) the loaded organic phase was first obtained from the finished extraction process; (2) the powder of extracted complex was obtained using the solvent-out crystallization with the anhydrous ethanol; (3) the wet powder was dried for 4 h at the temperature of  $353.2 \pm 0.1$  K in the blast drier; (4) the dry powder of extracted complex was used for the IR spectrum analysis (Fig. 7). Peaks in the extracted complex are analyzed as follows: asymmetric stretching vibration of - $CH_2$  (2917 cm<sup>-1</sup>), symmetric stretching vibration of  $-CH_3$ (2849 cm<sup>-1</sup>) (Suresh et al., 2016), in-plane bending vibration of -CH<sub>3</sub> (1458 cm<sup>-1</sup>) (Tayyari et al., 2016), the asymmetric and symmetric stretching vibrations of V = O (969 and 940 cm<sup>-1</sup>) (Nandi and Sarkar 2012), the stretching vibrations of V-O-V (721, 617 and 525 cm<sup>-1</sup>) (Zhang et al., 2016). Com-



Fig. 6 Slope method for the investigation of extractive mechanism.

pared with the IR spectrum of fresh TSIL of  $[C_{12}H_{25}NH_3]$ [Cyanex 272], there peaks of  $v_{sym}(-CH_3)$ ,  $v_{asym}(-CH_2)$ , and  $\delta$ (-CH<sub>3</sub>) in the extracted complex has been happened red shift, indicating the formation of new extracted complex.

# 3.6. Stripping for TSIL-based organic phase and its recycling use

When pH<sub>ini</sub> = 1.5, O/A = 2:1,  $C_1 = 0.26$  mol/L,  $T_e = 298$ . 2 ± 0.1 K, and  $t_e = 25$  min, the  $E_v$ ,  $E_{Cr}$  and  $\beta_{V/Cr}$  were about 99.5 %, 15.6 % and 1.08 × 10<sup>3</sup>, and the concentrations of V(V) and Cr(VI) in the loaded organic phase were about 23.58 and 0.30 g/L. The loaded organic phase containing V(V) and a small amount of Cr(VI) was first scrubbed twice using the fresh water (the volume ration of deionized water to TSIL-based organic phase was 0.5:1 for every time), and the loaded Cr (VI) in organic phase was almost completely removed using this process. After scrubbing, a dilute solution of  $NH_3 \cdot H_2O$  was used as a stripping agent to recover V(V) from the organic phase (Joo et al., 2016, Wei-Sheng and Hsing-Jung 2018), and the stripping reaction can be expressed as Eq. (13).

$$\begin{aligned} & [C_{12}H_{25}NH_3][Cyanex\ 272]_4 \cdot (H_4V_4O_{12})_{(org)} + 4NH_3 \cdot H_2O \\ & \leftrightarrows 4[C_{12}H_{25}NH_3][Cyanex\ 272]_{(org)} + 4NH_4VO_3 + 4H_2O \end{aligned}$$
(13)

Therefore, the influence of the stripping time  $(t_s)$  on the  $S_V$  is shown in Fig. 8a when the concentration of NH<sub>3</sub>·H<sub>2</sub>O ( $C_2$ ) is 0.42 mol/L, stripping phase ratio  $(O/A)_s$  is 1:1, and stripping temperature  $(T_s)$  is 303.2  $\pm$  0.1 K. The  $S_V$  increases with the growth of  $t_s$  when it is in the range of 10–40 min, and the  $S_V$  remains almost unchanged when the  $t_s$  is in range of 40–60 min. With the increase of  $t_s$  from 10 to 40 min, the  $S_V$  increases from 55.7 to 94.7 %. When  $t_s$  is changed from 40 to 60 min, the  $S_V$  keeps at the same value of 94.6 %. The stripping was basically reached equilibrium state when the  $t_s$  is 40 min, and this reaction time is the suitable condition for the process of stripping.

The effect of  $C_2$  on  $S_V$  is shown in Fig. 8b when  $t_s$  is 40 min,  $(O/A)_s = 1:1$ ,  $T_s = 303.2 \pm 0.1$  K. The  $S_V$  increase with the growth of  $C_2$  when it ranges from 0.33 to 0.61 mol/L, and the  $S_V$  is 99.2 % when  $C_2$  is 0.52 mol/L. The change of  $S_V$  is very small when the  $C_2$  ranges from 0.52 to 0.61 mol/L, and the increasing in basicity for aqueous solution will improve the recovery cost of the V-Cr slag. Therefore, the  $C_2$  of 0.52 mol/L is a reasonable concentration of NH<sub>3</sub>·H<sub>2</sub>O for the stripping process considering stripping efficiency.

To sum up, after scrubbing of the loaded organic phase, then it was stripped with the diluent NH<sub>3</sub>·H<sub>2</sub>O of 0.52 mol/L when  $(O/A)_s = 1:1$ ,  $T_s = 303.2 \pm 0.1$  K, and  $t_s = 40$  min. The recovered NH<sub>4</sub>VO<sub>3</sub> (Fig. 9) was obtained using the processes of stripping, filtration, washing, and desiccation (378.2



Fig. 7 IR spectra of extractant and extracted complex.



Fig. 8 Effect of  $t_s$  on  $S_V(a)$ ; Effect of  $C_2$  on  $S_V(a)$ .



Fig. 9 XRD patterns (a) and SEM (b) of recovered  $NH_4VO_3$ .

 $\pm$  0.1 K and 10 h) from the loaded organic phase. The XRD of recovered NH<sub>4</sub>VO<sub>3</sub> is shown in Fig. 9a, and the peaks are good consistent with the standard peaks. The SEM image of recovered NH<sub>4</sub>VO<sub>3</sub> is presented in Fig. 9b, and the plate-like crystals of NH<sub>4</sub>VO<sub>3</sub> are in an aggregate or homogeneous state. The separation and recovery of V(V) from Cr(VI) in aqueous solutions can be reached using the new extracted system including the novel TSIL of [C<sub>12</sub>H<sub>25</sub>NH<sub>3</sub>][Cyanex 272].

The TSIL-based organic phase containing V(V) and a small amount of Cr(VI) was first scrubbed twice using the fresh water, and TSIL-based organic phase containing Cr(VI) was almost completely removed using this process, and the organic phase containing V(V) was stripped with the diluent  $NH_3$ · $H_2$ -O, and the recovered  $NH_4VO_3$  was obtained from aqueous phase containing V(V). After stripping, the reusable TSILbased organic phase (about 97.2 % yield, Fig. 10) was obtained from the TSIL-based organic phase containing V (V), and this reusable TSIL-based organic phase can be reused for extraction of V(V) from simulated solution containing V (V) and Cr(VI). The recovered  $Cr_2O_3$  can be also obtained using the processes of evaporation, drying, dehydration, and calcination from aqueous phase containing Cr(VI) (Ying et al., 2020). The investigation on the recovery of Cr(VI) has not been further carried out in current experiments. In the next step of processing the actual leach liquor, the systematic research will be carried out in our laboratory. Here, the recycling method for Cr(VI) has been referred to the published article (Ying et al., 2020).



Fig. 10 Recycling use of TSIL-based organic phase [The process in the dashed line has not been carried out in this study, and this treatment process can be referred to the published article(Ying et al., 2020)].

#### 4. Conclusions

In this research, the novel TSIL of [C12H25NH3][Cyanex 272] was synthesized using the reaction of C12H25NH2 and Cyanex 272, and its qualitative analysis was made using the <sup>1</sup>H NMR, <sup>13</sup>C NMR and FT-IR spectroscopy. The efficient separation and recovery of V(V) from Cr (VI) has been studied using the new TSIL-based extracted system. The  $\beta_{V/Cr}$  was about 1.08  $\times$  10<sup>3</sup> when pH<sub>ini</sub> = 1.5, O/A =  $C_1 = 0.26 \text{ mol/L}, T_e = 298.2 \pm 0.1 \text{ K}$  and  $t_e = 25 \text{ min}$ , and the  $E_V$ was about 99.5 %. The product of recovered NH<sub>4</sub>VO<sub>3</sub> was obtained using the processes of stripping, filtration, washing, and desiccation from the loaded organic phase. The  $S_V$  was about 99.2 % when (O/  $A_{\rm s} = 1.1, T_{\rm s} = 303.2 \pm 0.1$  K,  $t_{\rm s} = 40$  min, and  $C_2 = 0.52$  mol/L. The recovered NH<sub>4</sub>VO<sub>3</sub> was further investigated by XRD and SEM, and the XRD peaks of recovered NH<sub>4</sub>VO<sub>3</sub> were good consistent with the standard sample, and its morphology was plate-like crystals. The extraction mechanism of V(V) using the [C12H25NH3][Cyanex 272] was studied using the slope method and FT-IR analysis, and the extraction mechanism is a complex reaction. This environmentally friendly process using the new TSIL can be used for the recovery of V(V) from real leaching solution for industrial application.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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